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LASER MEANS OF SYNTHESIZING AND MODIFYING
REFRACTORY POWDERS.

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Rept. for 1 Jul-30 Nov 77

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(11) 1 Jul 77

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ARPA Order No.: 3449
Program Code No.: NR039-153
Contract No.: (15) NR00014-77-C-0581
Contract Date: 1 July 1977
Contract Expiration Date: 30 June 1979
Contract Amount: \$256,580.00
Status Report Period: 1 July - 30 Nov., 1977

ARPA Order-3449

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Introduction

→ The objective of this program is to explore laser means of producing ceramic powders which exhibit superior densification characteristics in sintering and hot pressing processes. Three distinct processes are being investigated. These are: synthesizing powders from gas phase reactants heated by directly coupling the light to the reactants, producing homogeneous or composite particles by pyrolysing gas phase reactants onto laser heated powders, and modifying particle size and shape by dissociating the powder particles with the high intensity light. Analyses and limited experiments indicate that these processes have attributes which should permit small diameter, high purity spherical powders to be produced with controlled dopant levels and narrow particle size distributions. It is because these attributes are important for achieving high strength ceramic bodies that the processes are being investigated.

Status

The actual elapsed time during which efforts have been devoted to this program is approximately 3 months, because contractual negotiations were completed in mid-August, 1977, rather than the nominal July 1 starting date. We plan to submit the next two quarterly reports on a bimonthly basis to bring the reports and contract onto the same quarterly schedual.

During this report period, the program has been staffed to proposed levels, and the program is proceeding smoothly through its initial phases. The M.I.T. Energy Laboratory has also provided funds for a part-time Research Associate, who is supplementing our efforts on direct heated gas phase reactions. Specifically, we have designed and largely constructed the two apparatuses for particle size and shape modification, and for gas

phase reactions. Calculations on predicted particle heating rates have been extended beyond those given in the proposal. Feed powders have been prepared and characterization techniques have been reviewed and selected.

Powder Modification

The apparatus designed for particle size and shape modification and for depositing on laser heated particles is shown schematically in Fig. 1. The laser beam runs in the vertical direction and the particle trajectory is in the horizontal direction. The laser energy density on the particles is varied by positioning a 5-inch focal length lens relative to the particle path. The effective spot diameter can be varied continuously from 6 mm to approximately 1 mm, corresponding to power densities from 550-19,000 watts/cm². Particles are introduced through a 1 mm ID tubing which is positioned concentrically within a tube having the same diameter as the filter. Particles are introduced isokinetically by maintaining equal gas velocities in the two tubes. Particles are caught on a type AA Millipore filter which is supported in a standard 37 mm filter cartridge. The gas train shown schematically in Fig. 2 will permit gas velocities and chamber pressure to be manipulated independently over wide ranges.

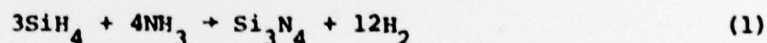
The chamber and optics for this apparatus are completely assembled and preliminary experiments have been initiated. Powders have been passed through the laser in an air atmosphere at various velocities. A controlled atmosphere powder feed apparatus has not been completed at this time. Qualitatively the powder temperatures observed at different velocities agree with predicted values. Experimental procedures and analyses require further development before they should be interpreted further. Comminution of Si₃N₄

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powders was not expected to follow predicted behavior in air atmosphere, because of the low vapor pressure of the SiO_2 protective skin, which is known to form with high oxygen partial pressures, and because of the N_2 ambient which suppresses vaporization. However, in a run where the injected Si_3N_4 particles obviously reached incandescent temperatures, the trapped particles exhibited two characteristic diameters. One corresponded to the injected powders ($\sim 30\text{-}40\text{ }\mu\text{m}$ diameter) and the others were approximately $3\text{ }\mu\text{m}$ in diameter. These experiments can only be interpreted when carried out in controlled atmosphere conditions.

Gas Phase Reactions

In the first direct coupling to gas phase reactants experiments, we will investigate the production of silicon nitride (Si_3N_4) from a reaction of silane (SiH_4) with ammonia (NH_3). In the reaction





after only 1.5 seconds of 50 W CO_2 radiation. Free silicon may be an efficient intermediate step for the production of silicon nitride. Yogeve et al⁽³⁾ found that the yield of the laser driven reactions they studied depended more strongly on the pressure than on any other parameter, including the intensity of the beam. In a situation where the absorbed energy merely heats up the gas, the rate of heating as a function of distance (d) depends on the pressure (P), the light intensity (I_0) and the absorption coefficient (α) via the relation:

$$\frac{dT}{dt} = \frac{I_0 (1 - e^{-\alpha dP})}{C_v dP}$$

Both reactions (1) and (2) can proceed thermally, i.e., the gas heats up until the reaction takes place, or molecules in excited vibrational states can react. We need to know what parameters determine the mechanism, and how the mechanism determines the product and the efficiency of the reaction. A direct measurement of α , the absorption coefficient, under low and high intensity irradiation will indicate the rate of energy dissipation under various conditions. The absorption coefficient, α , will change as the molecules become vibrationally excited due to asymmetry of the vibrational potential well. Precise knowledge of α should allow a good calculation of the rate of heating. A direct measurement of that rate will indicate the amount of energy staying in the vibrational manifold, and the rate of energy loss to the walls of the reaction vessel. Finally, a study of the dependence of the efficiency of reaction (2) versus pressure and I_0 should give a good idea of the conditions which will make reaction (1) proceed the most efficiently.

All of the above measurements will be made using a stainless steel reaction vessel now under construction, shown schematically in Fig. 3. Actual attempts to synthesize powders under flowing conditions will also be possible with minor modifications. The cell and associated tubing and valves are all stainless steel, since NH_3 is corrosive to aluminum and all copper compounds. It is 10.2 cm long, with an internal diameter of 2.5 cm, providing a useful internal volume of 51.5 cm^3 . The ends are sealed with 3.8 cm diameter KCl windows, mounted on O-rings for positive vacuum and high pressure seal. Access to the cell is by nine O-ring sealed 1/4 inch Swage lock fittings, to which can be connected thermocouples, leads to vacuum gauges or to the vacuum pump, or the gas inlets. For static experiments two or three thermocouples would be mounted at successive distances from the input window to monitor the temperature differences along the axis of the cell. At pressures around 1 atmosphere, most of the laser energy will be dissipated in the first centimeter of gas, so there will be a large thermal gradient within the 10 cm path length. The thermocouples can also be placed any distance from the center of the cell to right next to the wall to monitor energy conduction to the walls. If spectroscopic identification of the species produced in the reaction is desired, light can be collected directly from the hot zone through quartz light pipes inserted through the same fittings. Preliminary flowing experiments can also be conducted since a variety of flow conditions can be set up using the nine ports. If a long path length volume is needed, the rear window can be removed and a long thin wall tube attached. Fig. 3 shows how the apparatus will be arranged for most experiments. This configuration allows simultaneous monitoring of the incident laser energy, the absorbed energy, the rate of heating of the gas sample, and the degree of chemical reaction as

reflected by a pressure change. The vacuum system facilitates the maintenance of a clean reaction volume and allows operating at less than an atmosphere of pressure. Various inert buffer gases can easily be introduced to study their affect on the reacting system.

Materials

For the optical comminution studies, it was necessary to first prepare powders with a narrow size distribution, and then to characterize them with regard to size distribution, shape, phase content and surface chemistry.

For initial experiments, reaction bonded silicon nitride (from KBI-AME, Inc.) was crushed, ball milled with iron balls, leached in dilute HCl, washed and screened to size. The powders were separated into lots of 20-30 μm , 30-38 μm , 38-44 μm and 44-53 μm . SEM observations of the powders confirmed the particle size range and showed the powder particles to be of fairly high density (in the neighborhood of 70% as specified by the manufacturer). X-ray diffraction using the technique described by Gazzara and Messier⁽⁴⁾, indicated 72% α and 28% β silicon nitride with no detectible free silicon ($< \sim 1\%$). Further analysis will include shape analyses in an automated scan instrument, ir spectroscopy, Auger spectroscopy and oxygen analysis. Information is being collected on these techniques in preparation for pre-test and post-test analysis.

Other powders which have been prepared for future experiments are aluminum oxide, silicon carbide, and agglomerated silicon nitride (from KBI-AME, Inc.) containing 85% α phase, 14% β phase and 1% free Si. Powders on order for future testing are amorphous submicron silicon nitride, as well as densely sintered silicon nitride with a proprietary additive which will be crushed, ground and sized. All of the latter powders are from GTE

Sylvania Inc. The sub-micron powders will be tested for chemical and phase modification, since our calculations show that little comminution will take place in this size range.

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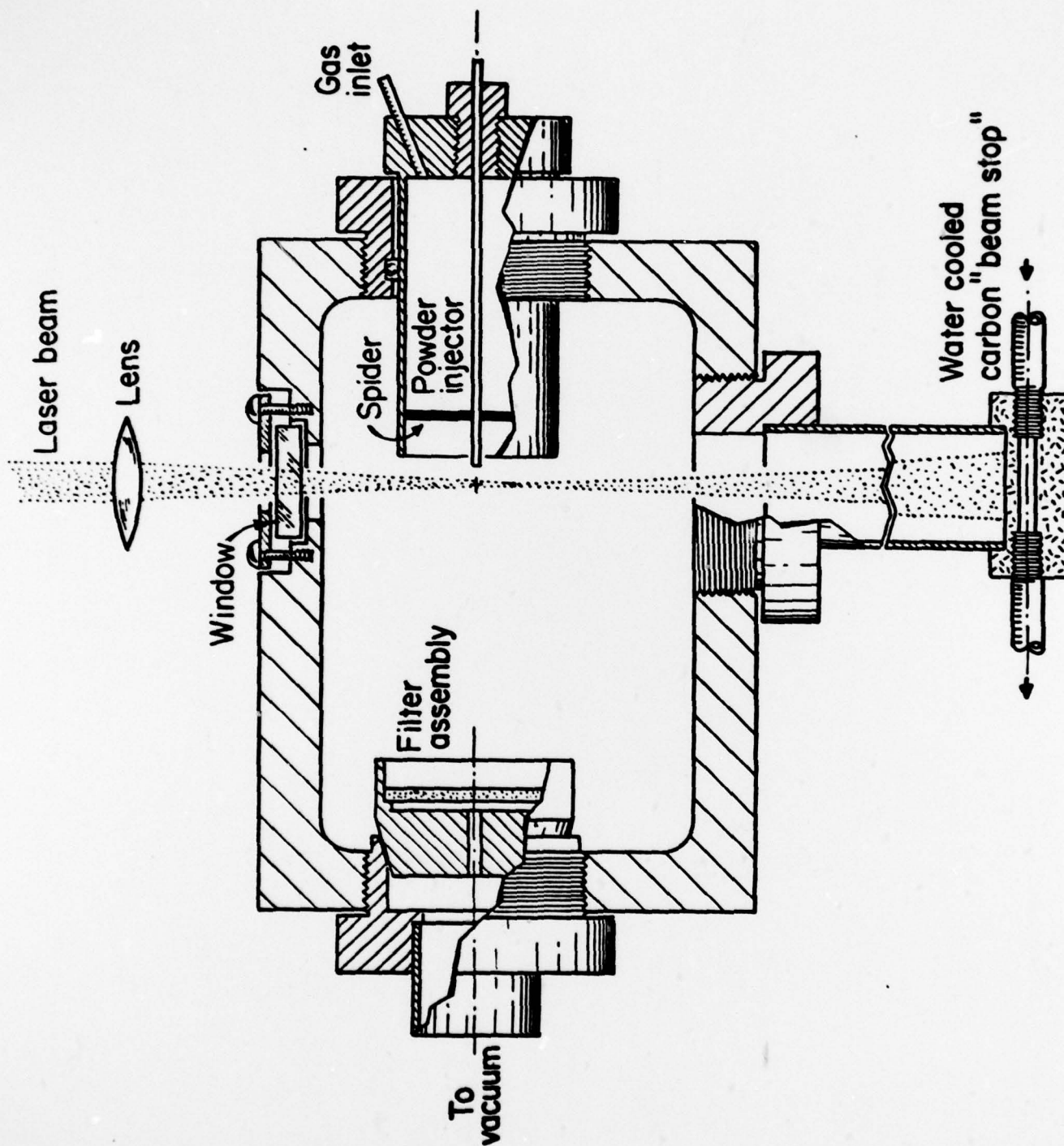


Figure 1. Chamber for powder modification experiments.

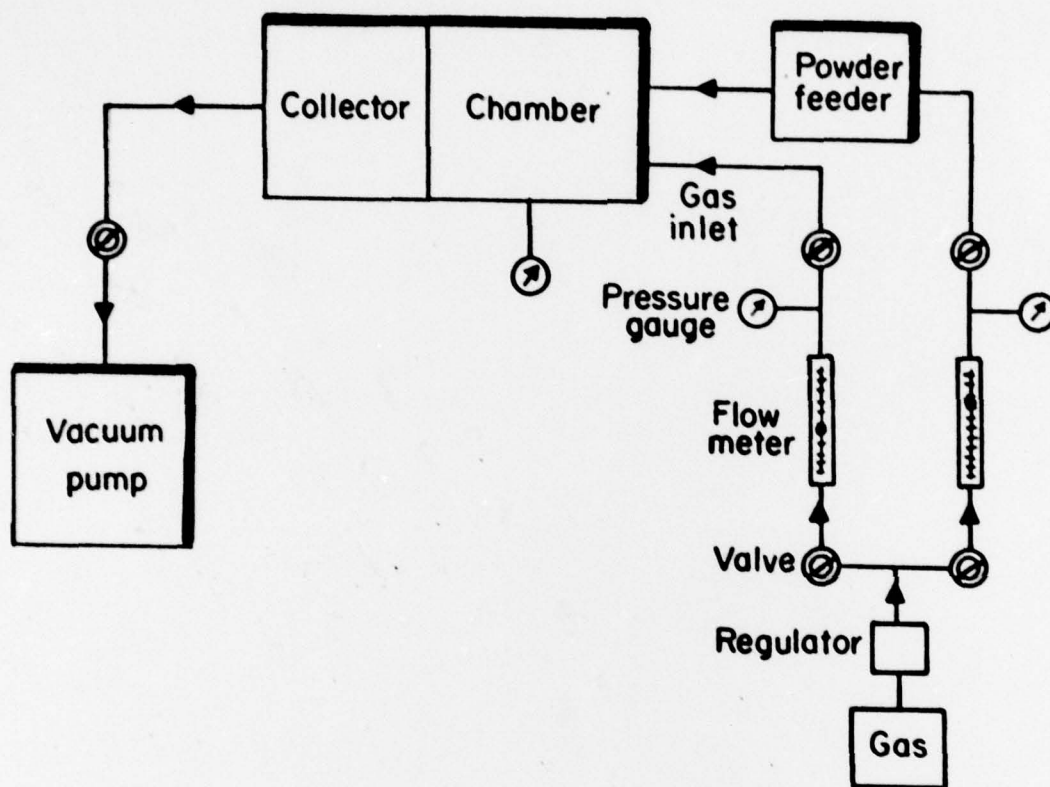


Figure 2. Schematic of gas train for powder modification chamber.

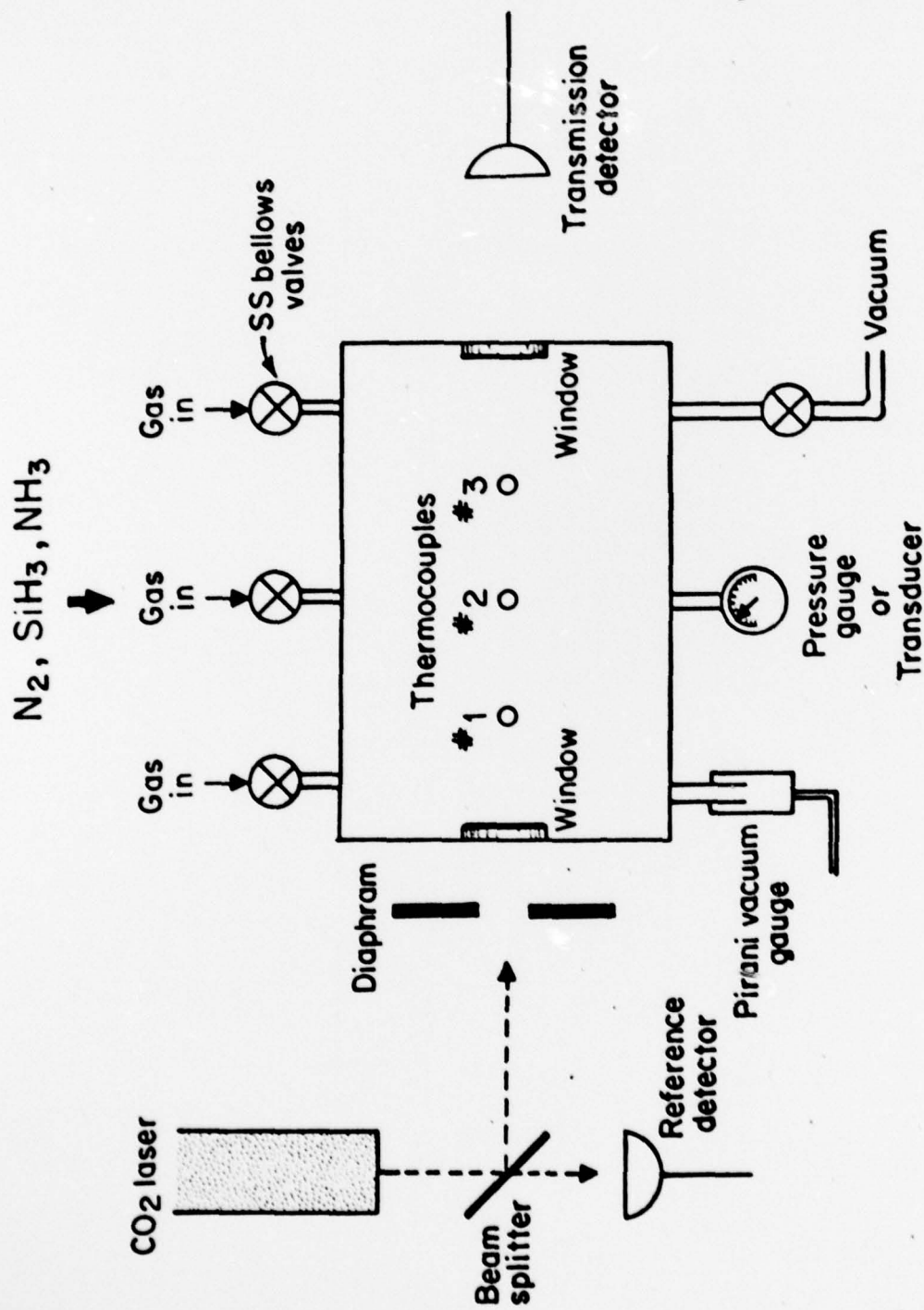


Figure 3. Schematic of gas phase reaction chamber and accompanying optical system.